

PATENT SPECIFICATION

DRAWINGS ATTACHED



924,497

Date of Application and filing Complete Specification July 3, 1959.

No. 23005/59.

Application made in Sweden (No. 6451) on July 5, 1958.

Complete Specification Published April 24, 1963.

Index at acceptance:—Classes 82, A1, A8(A1:A3:H:Q:U:W:Y), A8Z(2:4:9:12), A11, F1G1, F2(F:M:Z2:Z4), F4X; and 95, B4(B:C:X).

International Classification:—B23u, C22c, C23c (B05).

COMPLETE SPECIFICATION

Improvements in or relating to Sintered Electric Resistance Heating Elements

We, AKTIEBOLAGET KANTHAL, a Swedish Company, of Hallstahammar, Sweden, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to sintered materials and products thereof, and more specifically it has for its object to provide a sintered material of high mechanical strength which is oxidation-resistant at high temperatures and has favourable electrical characteristics making the material particularly adapted for use in electric resistance heating elements to be operated in non-inert atmospheres and at high temperature.

A resistance heating element according to the invention consists—in its high temperature part, at least—of a sintered body which is composed of a metallic alloy component containing at least molybdenum, silicon and aluminium, and, optionally, of a comminuted ceramic component. A characteristic feature of the metallic component resides in that its composition should always satisfy the basic formula $(\text{Mo}_{1-y}\text{M}_y)(\text{Si}_{1-x}\text{Al}_x)_z$, where M represents one or more of the metals Ti, Zr, Hf, Ta, Nb, V, W and Cr, and where x may range from 0.1 to 0.6 and the upper limit of y may range up to 0.7 and in that its crystal structure is of the type C 40. As will be more closely described below, the upper limit of y may be different for different metals M. For the system of lattice notations used in this specification see for example textbook entitled "Refractory Hard Metals" 1953, issued by Kiefer and Schwartzkopf.

It is a well known fact that silicon-containing protective coatings or skins on molybdenum silicide surfaces will be improved if

[Price 4s. 6d.]

aluminium is also included in the coating. Such improvement is considered to result from the feature that the oxide coating forming in atmospheric air at high temperature would not consist of silicon dioxide only, but also of an aluminium silicate, such as mullite, for example, which is assumed to possess more advantageous characteristics.

Pure MoSi_2 crystallizes according to the tetragonal lattice type C 11, whereas the metallic material according to the present invention crystallizes according to the hexagonal lattice type C 40. The lattice constants of the C 40 phase within the scope of the invention vary according to the composition. For $y=0$ the following ranges of values of the lattice constants, a and c were obtained:—

a : 4.65 to 4.76 kx

c : 6.53 to 6.57 kx

in which kx is a unit corresponding to 10^{-3} millimeters.

The substitution of Al for Si in the formula $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_z$ will thus cause the lattice to expand due to the fact that the aluminium atom is larger than the silicon atom. Similarly, the substitution of M for Mo will cause lattice expansion if M is W, Ta, Nb, Ti, Zr or Hf, and lattice contraction if M is Cr or V.

It has now been found, quite surprisingly, that said metallic material of the C 40-lattice type possesses electrical characteristics which are more advantageous than those of MoSi_2 and further has good oxidation resistance and mechanical strength provided the C 40 phase is the single component that possesses metallic electrical conductivity.

The invention will be more closely described with reference to the accompanying drawings, given by way of example, in which Figs. 1 to 10 are diagrams.

Fig. 1 of the accompanying drawings shows

Best Available Copy

how the resistivity r varies as a function of the temperature $t^{\circ}\text{C.}$ for MoSi_2 having C 11 structure (curve A) and for an alloy according to the present invention (curve B) having C 40 structure and the composition: $\text{Mo}(\text{Si}_{0.8}\text{Al}_{0.2})_2$. In both cases the specimens were poreless and consisted exclusively of crystals of C 11 and C 40-type respectively. For MoSi_2 , the resistivity increases within the range 20°C. to 1600°C. from 0.23 to 3.2 ohm $\text{mm}^2/\text{m.}$, i.e. by 1400%, whereas the alloy according to the present invention exhibits an increase from 1.2 to 5 ohm $\text{mm}^2/\text{m.}$, i.e. by 315% only. It is of great importance in practice to be able, by a comparatively slight change in the chemical composition of molybdenum disilicide, to obtain a product of the C 40 crystal type having a resistivity which, at all practical temperature, is at least four times as high as that of pure MoSi_2 . This has made it possible for the first time, without the aid of any oxide additions, to produce resistance elements on a molybdenum silicide basis and in which the heating zone and the cool terminal end portions are of identical, or nearly identical, cross-sectional areas. As a matter of fact, if the terminal end portions consist of pure MoSi_2 , the cooling effect caused thereby will be sufficient to make unnecessary any impractical and costly enlargement of cross-sectional area of the terminal end portions of the element. The specific resistance r as a function of temperature for such a combination of crystals of C 40-type and an oxide component is shown in Fig. 1, curve C. The lowered thermal coefficient of electrical resistivity of the resistor of C 40 alloy type is, of course, another advantage of great practical and economical importance, particularly in connection with large furnace plants.

A further advantage of elements according to the invention resides in that their mechanical strength is higher than that of elements of MoSi_2 which fact, of course, is of great importance where inherently brittle materials are concerned. The strength characteristics of the material can be further improved by the use of suitable binders, such as binders containing at most 40% by weight of SiO_2 and a balance of substantially Al_2O_3 in a highly comminuted condition, and preferably in glass-form, i.e. any type of glass or enamel having in addition to SiO_2 , an amount of Al_2O_3 as a constituent.

Contrary to previous statements, we have found that the oxide coating which forms on the surface of Mo—Si—Al -alloys of the kind described will not show as satisfactory characteristics as does the pure quartz glass forming on molybdenum disilicide. Therefore, according to the present invention, it is contemplated to add a small portion of boron in one form or another which will impart to the protective coating a more glass-like struc-

ture and more favourable characteristics than those obtaining for the mullite-containing glaze forming on the resistance elements in the absence of boron. Such boron may be added to the alloy proper, or it may be included by adding borides, borates or boric acid in the powder-metallurgical process of producing the material. Since the amount of boron thus added should be small, at most 0.3% by weight of the sintered body, it has not been possible to state just in which form the boron is contained in the final product. Thus it is conceivable that the composition of the C 40 phase, $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$ may have been slightly modified by a slight amount of silicon or aluminium having been replaced by boron.

The composition of Mo—Si—Al alloys contained in resistance elements according to the invention will appear from Fig. 2 of the accompanying drawings showing a triangular graph plotting the percentage weights of molybdenum, silicon and aluminium contained in the material. For the purpose of comparison, this graph also includes the compositions of previously known alloys containing molybdenum, silicon and aluminium. The hexagon A—B—C—D—E—F represents the area covered by alloys previously known and constituted by 20 to 80% Mo, 0 to 30% Al and 10 to 70% Si. The triangle G—H—I represents the area covered by the British Patent Specification No. 731,616 which has the same origin but differs from the U.S.A. Patent Specification No. 2,831,242 to Kieffer et al. This U.S.A. specification covers electric resistance materials produced by sintering 60 to 70 parts by weight of molybdenum and silicon in proportions corresponding stoichiometrically to MoSi_2 , and 10 to 30 parts by weight of molybdenum and aluminium in proportions corresponding to MoAl_3 . The possible range of variation of the composition of the silicide-aluminide component according to Kieffer is represented in the graph of Fig. 2 by the line N—O, forming part of the line K—M, where K corresponds to the composition MoSi_2 and M corresponds to the composition MoAl_3 . On the other hand, alloys containing Mo, Si and Al in accordance with the present invention are to have a composition corresponding to the line K—L, i.e. corresponding to the formula $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$.

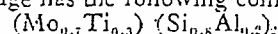
It has been noticed, as a result of experiments carried out in connection with the present invention, that upon sintering mixtures of molybdenum, aluminium and silicon in proportions corresponding to points along the line K—M, a mixture of several phases are obtained, including, *inter alia*, a molybdenum-silicide-aluminide of a basic composition corresponding to $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$ and which crystallizes according to the C 40-lattice type. For example, for an alloy located at point N one constituent was found to be a composition corresponding to a value of $x=0.2$

in the above formula. It is self-evident, however, that aluminium or substances rich in aluminium must be present besides the C 40 lattice type since the total content of (Al+Si) is larger than that corresponding to the formula $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$. If a material of the above-stated composition is to be used for electric resistance elements to be operated in an oxidizing atmosphere at high temperature, the presence of such less oxidation-resistant aluminium-containing impurities will involve a degradation of the overall characteristics of the alloys produced.

Also compositions located along the line K—L, i.e. between the points of MoSi_2 and MoAl_2 , have been investigated in connection with the present invention. Such investigation has shown that sintering of molybdenum, silicon and aluminium in these proportions at 1300° in hydrogen will not create a pure C 40 structure but rather a mixture of C 40 with other phases, inter alia Mo_3Si_5 . Also such mixtures have been found to be less suitable as electric resistance materials for high-temperature operation. It has generally been established by several tests run with mixtures of molybdenum, silicon and aluminium in quite different proportions, that it is very difficult to obtain a pure C 40-phase. Without being restricted to our theory, we would interpret these test results by the assumption that an amount of aluminium in excess is able to enhance the formation of the desirable C 40-phase $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$. This excess of aluminium should be of a size such as to cause the composition of the mixture to be located along the line O—H in Fig. 2. The C 40-phase thus obtained may have the non-desired aluminium in excess removed from it by leaching with an acid and the rest consisting of pure C 40-phase may or may not be mixed with a binder and thereafter sintered in a conventional manner into resistance elements. If the aluminium content of the acid-leached pure C 40-alloy should still be too high it may be "diluted" before the sintering step by adding pure MoSi_2 to the mixture. Thereby the value of x in the formula $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$ can be reduced from the range 0.3—0.6 to the range 0.1—0.3. In Fig. 2 different values of x have been inserted at points P_1 to P_n , the point P_1 representing x=0.1, P_n representing x=0.2, up to P_n representing x=0.6.

According to a specific embodiment of the present invention it has been found, quite surprisingly that an addition of moderate amounts of one or more of the remaining transition elements of Groups IV, V and VI of the periodic table may overcome the above-mentioned difficulties, thus making it possible by direct sintering of the initial material in comminuted form without acid-leaching to produce a pure C 40-phase which is excellently suited as an electric resistance material for high temperature operation in air. It has been found by

X-ray crystallographical examination that the metals (M) added will partially replace the molybdenum in the composition $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$, i.e. according to the formula: $(\text{Mo}, \text{M})(\text{Si}, \text{Al})_2$. It has been found particularly advantageous to add metals of the kind forming disilicides which crystallize according to the C 40-lattice type, i.e. Cr, Ta, Nb and V. Nevertheless it is possible, however to obtain the corresponding effect by an addition of other metals the disilicides of which do not crystallize according to the C 40-lattice type, for instance W, Zr, Hf and Ti. An addition of TiSi_2 to pure MoSi_2 , as previously known, will give rise to a C 40-phase, and therefore Ti is used in alloys according to the present invention. One such alloy which may be used to advantage has the following composition:—



The addition of the metal (M) should be adapted to the results desired and also depends on the value of x. It has been found as a result of practical experiments that a stable, pure C 40-structure will be obtained if up to 70 atom percents of the molybdenum contained is replaced by another metal, where the upper limit depends on the kind of metal added.

It should be mentioned that in Specification No. 791,323 we state that a product of the reaction between 40% of TaSi_2 and 60% of MoSi_2 will yield a pure C 40-phase of the composition $(\text{Mo}, \text{Ta})\text{Si}_2$. Practical experiments have shown, however, that this product exhibits insufficient resistance to thermal shocks which makes the same unusable for electric resistance heating elements which are subjected to violent temperature changes. The material of the present invention distinguishes from this material, as well as from other mixed disilicides of the C 40-type, in that it has been found to be well adapted for operation at 1700° C. in air and to withstand stresses of any kind encountered under operating conditions. In addition, the material exhibits the low thermal coefficient of electrical resistivity characteristic of certain C 40-structures. Thus alloys according to this aspect of the invention should include products of the composition $(\text{Mo}_{1-y}\text{M}_y)(\text{Si}_{1-x}\text{Al}_x)_2$, where x ranges from 0.1 to 0.6, M may be any one of the elements Ti, Zr, Hf, V, Ta, Nb, W and Cr, and y ranges from zero to 0.70.

A resistance element according to the invention preferably comprises an incandescent or heating zone and two terminal end portions, the silicide component of said incandescent zone being constituted by an alloy according to the present invention, whereas that of the terminal end portions preferably consists of pure MoSi_2 . Both the incandescent zone and the terminal end portions may optionally include 50% by volume, at most, of a comminuted ceramic component, preferably a glass containing SiO_2 . Falling within the scope

of the invention are also resistance elements produced by so-called flame spraying, or spray metallization, for example, and in which the incandescent zone is formed by a layer having a thickness of 10 to 500 microns and applied to an insulating refractory base member:

Elements according to the present invention may be produced in several different ways, as will appear from the following examples:—

EXAMPLE 1.

A pulverulent mixture of by weight 6% Ta, 60% Mo, 26% Si and 8% Al is heated in hydrogen at 1300° C. As a result of an exothermic reaction a spongy product will form and by X-ray analysis it was found to consist exclusively of a C 40-alloy having the composition: $(\text{Mo}_{0.95}\text{Ta}_{0.05}) (\text{Si}_{0.76}\text{Al}_{0.24})_2$.

The alloy is ground in a ball mill into a grain size less than 10 microns and is mixed with 5% by weight of plasticized bentonite in a vacuum kneader. The mass is extruded into a round wire 7 mm in diameter which is dried and subjected to pre-sintering in hydrogen gas at a temperature between 800 and 1400° C. Final sintering then takes place during 2 minutes by passing electric current directly through the wire in air at 1500 to 1700° C. The terminal end portions are produced in a similar manner and are of substantially the same cross-sectional areas as the incandescent zone, but in this case, besides bentonite, a powder exclusively of molybdenum disilicide is used. After face grinding the ends of the incandescent zone and terminal end pieces these are sintered together by electric butt welding. Subsequently the terminal end portions of the resistance element formed are equipped with terminal contacts, for instance of aluminium, which do not require additional cooling owing to the great difference in resistivity as between the two alloys of the terminal end portions and the incandescent zone respectively. If the length of the incandescent zone is 500 mm and that of each terminal end portion is 250 mm, the total weight of the element will only be 162 g. On the other hand, if the incandescent zone as well as the terminal portions were based on MoSi_2 instead of the silicide alloy, it would have been necessary to produce terminal end portions having a cross-sectional area four times as large would be have resulted in a total weight of 410 g. for the resistance element.

EXAMPLE 2.

According to a specific embodiment of Example 1 it is suitable to add to the expanded bentonite a solution containing boric acid amounting to 0.01% by weight of the powder mixture. This will involve the favourable result that, in the step of sintering the incandescent zone, the ceramic component and the protective surface layer obtaining due to oxidation, will contain, in addition to SiO_2 and

Al_2O_3 , also small amounts of B_2O_3 , which will result in an advantageous increase in mechanical strength of the resistance element.

EXAMPLE 3.

A powder mixture of by weight 53% Mo, 18% Si and 29% Al (point R in Fig. 2), i.e. in proportions corresponding to one part by weight of MoSi_2 and one part by weight of MoAl_3 , is reacted in hydrogen at about 1300° C. and is then crushed into a particle size less than 50 microns. The powder is leached for 5 minutes with cold diluted (1:10) hydrochloric acid, dissolving substantially aluminium. On X-ray analysis the remainder was found to be a material of the C 40-lattice type corresponding approximately to the formula: $\text{Mo}(\text{Si}_{0.8}\text{Al}_{0.2})_2$. After the leaching step one part by weight of the powder is mixed with two parts by weight of a powder of MoSi_2 and is ground in a ball mill until 90% thereof have a grain size less than 6 microns. Then the mixture is shaped and sintered in the same way as according to Example 1. A chemical and X-ray analysis of the alloy of the final product shows that it will crystallize completely according to the C 40-lattice type and has the composition by weight: 63% Mo, 30% Si and 7% Al corresponding to $\text{Mo}(\text{Si}_{0.8}\text{Al}_{0.2})_2$ (point P₂ in Fig. 2). It will be possible to carry out leaching even if up to 70 atom percent of the Mo has been replaced by the metals M.

EXAMPLE 4.

A pulverulent mixture of by weight 10.5% Ti, 49.0% Mo, 8% Al and 32.5% Si was heated in hydrogen gas at 1300° C. The product of the reaction was treated as in Example 1 and resulted in a resistance element in which the alloy of the incandescent heating zone had the composition $(\text{Mo}_{0.7}\text{Ti}_{0.3}) (\text{Si}_{0.8}\text{Al}_{0.2})_2$.

EXAMPLE 5.

The pulverulent mixture had the composition by weight: 6% Ta, 60% Mo, 25.7% Si, 8% Al and 0.3% B. Resistance elements were produced as in Example 1. A slight amount of boron is oxidized in the final sintering of the incandescent zone and is included both in the ceramic component and in the protective surface layer.

EXAMPLE 6.

A sillimanite rod $\frac{1}{2}$ " in diameter was coated by flame spray metallization with a layer 50 microns in thickness and of the composition $(\text{Mo}_{0.95}\text{Ti}_{0.05}) (\text{Si}_{0.7}\text{Al}_{0.3})_2$. The terminal end portions of the element were of the identical composition but with a surface coating thickness of 200 microns. The spray metallization was carried out with a conventional spray gun and using a wire containing 15% polythene, 4% aluminium powder and 81% molyb-

denum silicide powder of a grain size less than 6 microns.

In respect of a silico-aluminide of Mo having C 40 structure and having aluminium substituted for 20 atoms % of silicon ($x=0.2$, $y=0.05$) the variation of its specific resistance measured in ohms/m mm² as a function of the temperature t° C. may be seen from Fig. 1, curve B, relating to this alloy in a poreless and oxideless state.

In Fig. 3 the resistivity obtained at room temperature in a series of tests of sintered bodies have been recalculated to the hypothetical resistivity of a poreless, oxideless alloy, which constitutes that component of the sintered body which possesses electrical conductivity of metallic character. These values have then been plotted as a function of the aluminium content of the alloy in % by weight. The specific electric resistance of the alloy at 20° C. rises then from about 0.25 for MoSi₂ to about 1.4 at a content of 16% Al ($x=0.43$). It decreases then towards 1.0 at 20% Al ($x=0.54$). Within the range of 8 to 20% Al ($x=0.21$ to 0.54) it is considered that the alloy consists of crystals of the pure C 40-type.

In Fig. 4 the specific resistance at 20° C. is plotted as a function of the Al-content of a sintered body which, in addition to the alloy Mo(Si_{1-x}Al_x)₂, contains by weight 19.2% aluminium oxide (tonerde) and 0.8% Fe. As the specific resistance at 20° increases with increasing aluminium content it holds true that, in respect of the temperature coefficient of the resistance counted as the ratio or quotient of the resistance at 1600° C. divided by the resistance at 20° C. this coefficient will, on the contrary, fall rapidly according to Fig. 5 which illustrates the fact how the temperature coefficient depends on the content of aluminium in sintered bodies which, in addition to the alloy, include 19.2% alumina clay (tonerde) and 0.8% Fe in a very finely divided condition. At higher content of aluminium it is apparently possible to rely thereon that the temperature coefficient defined as above is only 2 which thus means a sharp reduction of the value obtained at a normal MoSi₂ body having a coefficient of about 12. It should, however, be pointed out that the dependency of the resistance on the temperature at varying aluminium contents affords an irregularity in the range of 8 to 12% Al as illustrated in Figs. 4 and 5. For the time being no explanation could be given to this irregularity but reference is made to the fact that a similar irregularity also occurs in X-ray crystallographical examinations of structures.

Above it has been pointed out that in X-ray crystallographical examinations of the hexagonal lattice it has been found that the lattice constants are altered when aluminium is substituted for silicon. The extreme values for the a-axis were determined to be 4.65 to 4.36

and for the c-axis 6.53 to 6.57 kx. A close examination of the variation of the axes depending on the quantity of added aluminium indicated that the a-axis is increased rather regularly from a minimum value of 4.63 to a maximum value of 4.75 kx when the aluminium content was increased from 6 to 20%. On the other hand, the c-axis follows a queer course which, for the rest, also varies with the performance of the sintering process and the composition of the oxide component. Thus in one case it was observed that the c-axis at 6% aluminium content was 6.65 kx and that it decreased to 6.53 kx when the aluminium content was raised to 10% and then again started to rise to a maximum of 6.60 at about 15% Al and then again started to fall down to reach the value 6.57 at 20% Al. At another composition of the oxide component the c-axis was found to be nearly constant as 6.54 kx at additions of from 6 to 16% Al whereas this axis then started to rise up to 6.57 kx at 20% Al. Also in this case it has not been possible to give any strict explanation of the irregularity but it has probably something to do with the fluctuations of the temperature coefficients of the electrical resistance.

Experiments carried out with a view to manufacture dense sintered bodies based on the above defined alloy have proved that the ceramic binding means should not contain a too high content of SiO₂. Probably this is related with the fact that the aluminium atoms in the silicide component are able at a high temperature to react with the silica of the binding means while forming aluminium oxide and silicon. In trials in practice it has also been found that the aluminium content of the silicide component is decreased if such sintered bodies are heat treated.

On the other hand, trials have been made to use aluminium oxide as binding means and it has then been proved that it is suitable to use slurries of particularly finely divided γ -Al₂O₃, for instance of the type used for polishing purposes and called "tonerde".

To facilitate the sintering to produce a low porosity it is suitable to let about 20% of the weight of the material be constituted by this tonerde as binding means, partly replaced by bentonite as the case may be. Trials have been made to mix tonerde with bentonite and it has then been found suitable to use the same quantity tonerde as bentonite. Apparently the ceramic component will then contain a comparatively low concentration of SiO₂ and any detrimental reaction with the aluminium of the silicide component could not be noticed. In heat treating such sintered bodies in a technically pure protecting atmosphere of a moderate temperature a small quantity SiO₂ is formed as in case of sintering MoSi₂ and the oxide component will then generally contain a small quantity of SiO₂ even if this was not added

from the beginning as binding means. The final composition of the oxide component may thus be from zero to 40% by weight SiO_2 and the balance Al_2O_3 together with other oxides, preferably of the type having a higher heat of formation than Al_2O_3 . The reaction between binding means having a high content of SiO_2 and the aluminium content of the silicide component may also appear from Fig. 10 in which the content of crystals of C 40-type of the alloy is plotted as a function of the quantity of added aluminium in the silicide component in respect of three different sintered bodies. In the curve A there are used 20% bentonite as binding means, in curve B 5% bentonite and 15% tonerde and in curve C 20% tonerde. When bentonite alone is used as binding means about 20% aluminium is required to form solely crystals of C 40-type whereas in the two remaining cases it is indicated that only 10% Al is necessary to form the C 40-type. In both these cases the quantity of SiO_2 in the binding means has been insufficient to remove any larger quantity of Al from the silicide component.

It may be assumed that the ratio between the Al_2O_3 and SiO_2 contents obtained in the oxide formed at a light oxidation of C 40 powder should be about that ratio that gives a chemical balance between the silicide and the oxide component. In this way the correct composition of the ceramic component could be foreseen.

Such a test has been carried out on a powder having 15% Al according to formula $\text{Mo}(\text{SiO}_{0.6}\text{Al}_{0.4})_2$ and an analysis of the oxide component gave 30% SiO_2 , 60% Al_2O_3 and a balance, probably substantially MoO_3 and smaller quantities of other oxides. At a lower Si content in the alloy the SiO_2 content of the oxide component may rise up to 40%.

Molybdenum silicide containing aluminium is considerably more difficult to sinter to a poreless product than, for instance, pure MoSi_2 . If a powder of, for instance, pure MoSi_2 having an average grain size of 43 microns is sintered 30 minutes at 1500° in hydrogen gas, there is obtained a shrinking of 12% by volume. If instead a molybdenum silicide powder is used containing 6% Al the corresponding shrinking will be only 1%. At higher Al contents the sintering will be somewhat improved, for instance, at 16% aluminium, 6½% shrinking. In both these cases 10% tonerde was used as binding means.

If instead bentonite is used the result will be slightly better but still a high temperature and a long sintering time are required to obtain a product with low porosity and mechanical strength. It has now been found that an addition of small quantities of ferrous sulfide to the tonerde will facilitate the sintering to a high degree. If the added quantity of ferrous sulfide is 0.5% of the weight of the sintered body the shrinking at a content of

6% Al will be 5% and at 16% Al 11%. If the addition of ferrous sulfide is only 0.05% still a considerable improvement is obtained, for instance, at 6% Al the shrinking will be 2.5% and at 16% Al 10%. In comparison with a material composed of MoSi_2 plus bentonite, however, a considerably higher sintering temperature and a longer sintering time will be required in the cited examples. This is indicated, inter alia, thereby that a sintering at 1400° C. produces a shrinking in respect of MoSi_2 plus bentonite of 9% but only 2.5% in respect of the aluminium containing product. At 1500° C. the corresponding values are 10% and 5.5%.

Also other additions have an advantageous influence on the porosity, such as small additions of iron, nickel, cobalt or their oxides, sodium fluoride and magnesium fluoride.

In practical efforts to extrude and sinter resistance elements containing the new aluminium containing alloy, it has been found that a sintering in air is difficult to carry out and requires a careful preceding heat treatment of the material for a sufficient time in hydrogen gas. The final sintering temperature must be kept higher than in respect of MoSi_2 and it should be above 1600° , preferably 1700° C. To avoid an unsuitable oxidation the heating up to the sintering temperature should be made very quickly, preferably on a time less than 30 seconds. It has been possible to weld a piece of an alloy of C 40-type onto a piece of an ordinary alloy of C 11-type the bending strength of the welded joint being then 16 Kgs/mm².

In the manufacture of resistance elements having terminals of MoSi_2 and an incandescent zone of an aluminium containing silicide the composition of the latter silicide should preferably be 12% Al, 24.5% Si and 63.5% Mo ($x=0.33$) being intermixed with 8% tonerde and 7% bentonite as binding means. Such elements may be used continuously at the same temperatures as the elements of pure MoSi_2 plus bentonite, i.e. up to 1700° C.

The pure C 40-phase in the system Mo—Si—Al, interbonded or not by means of an oxide component, complies thus in an excellent way with the requirements on an electrical resistance element for high temperatures. A condition is, of course, that beyond its oxide component this element only contains metallicly conducting particles of pure C 40-phase.

Below three examples of test series of alloys are cited. In each case the alloys have been produced as follows. The entering metals are mixed in correct proportions and heated in hydrogen gas until a complete reaction has taken place. The reaction product is crushed and then milled during 120 hours in a ball mill so that an average grain size of about 3 to 7 microns is obtained. The powder is intermixed with tonerde and, as the case may be,

bentonite and water, kneaded in vacuum, extruded, dried and sintered, at first to 1400° C. in hydrogen gas and then to 1700° C. in air.

- 5 Figs. 6 and 7 indicate variations in two important properties of two series of materials in which, on the one hand, Zr and, on the other hand, Ta is substituted for a fraction of the Mo content. In Fig. 6 the ordinate is for tensile strength and in Fig. 7 for percentage by volume porosity.

EXAMPLE 7.

- 15 In respect of Zr it was ascertained through X-ray crystallographical examination that other phases than C 40 begun to occur when y in the formula $\text{Mo}_{1-x}\text{Zr}_x(\text{Si}_{1-x}\text{Al}_x)_2$ exceeded a value of 0.2. Of Fig. 6 it appears now clearly the advantage of the addition of the alloy substance Zr when a higher mechanical strength is required and also the disadvantage of exceeding the limit of solubility which limit in the case of Zr is at $y=0.2$. When passing this point there will be a sudden decrease in the mechanical strength. Another important property in connection with oxidation proof resistance material is its compactness or degree of porosity both from the point of view of mechanical strength and from the point of view of the resistance against oxidation attacks because a porous body has a greater surface exposed to oxidation than a poreless body and this porous body must necessarily be aged much quicker than the poreless body. According to Fig. 7 the addition of Zr has a very favourable influence on the compactness up to the limit of solubility at $y=0.2$ whereupon an increased addition of Zr results in a pronounced increase in porosity.

EXAMPLE 8.

- 40 According to this example Ta was added according to the formula $(\text{Mo}_{1-x}\text{Ta}_x)(\text{Al}_{1-x}\text{Si}_x)_2$ and through X-ray crystallographical examination it was ascertained that other phases than C 40 started to appear when y in the formula exceeded 0.7. In Fig. 6 it is shown how the tensile strength increases with an increased Ta content up to $y=0.7$ and then again decreases. Fig. 7 indicates that the Ta-addition has no appreciable influence on the porosity of the material until the limit of solubility at $y=0.7$ is passed when the porosity will rise very steeply.

EXAMPLE 9.

- 55 Finally the corresponding two properties are illustrated in Figs. 8 and 9 in respect of a mixture of $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$ and $\text{Mo}_2\text{Al}_6\text{B}_2$ in which the solubility of boron in $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$ is very low, i.e. corresponding only to a few % by weight of $\text{Mo}_2\text{Al}_6\text{B}_2$ or a few tenths % by weight of B. Also from these figures it will be quite clear that the properties deteriorate when the two phases

are mixed. Any larger amounts of boron should accordingly be avoided. In Fig. 8 the ordinate is for tensile strength and in Fig. 9 for percentage by volume porosity.

It was also ascertained by ageing tests that in all three Examples 7 to 9, the resistivity against oxidation attacks of the pure C 40-phase was satisfactory and that as soon as there was a pure C 40-phase the ratio between its specific resistances at 1600° C. and 20° C. was between 1 and 6 which makes the material quite suitable as electric resistance material.

75 In our Patent Specification No. 899,464 we have claimed a thermo-couple which is suitable for use at elevated temperatures in oxidizing atmospheres, having at least one leg which comprises a thermo-electric molybdenum disilicide alloy having the crystal structure C 40 (CrSi_2 -type) in which 20—60 percent of the silicon atoms have been substituted by aluminium atoms. The said specification also claims a thermo-couple as set forth above, in which the thermo-electric alloy is of the composition $(\text{Mo}_{1-x}\text{M}_x)(\text{Si}_{1-x}\text{Al}_x)_2$, wherein M is one or more of the metals Ti, Zr, Hf, Nb, Ta, V, W, Cr, x is between 0.2 and 0.6 and y is between 0 and 0.5. The said specification also states that the thermocouple may also be used as a heating resistor for producing high temperatures, serving as a thermo-couple for short periods when thermo-voltage is measured and serving as an electrical heating resistor for the remaining periods. No claim is made in the present specification for a thermo-couple as claimed in Specification No. 899,464.

Subject to the foregoing disclaimer, what we claim is:—

100 1. An electric resistance heating element which consists, at least in a high temperature part thereof, of a sintered body having metallicly conducting particles therein constituted by silico-aluminide forming a pure phase with crystals of the lattice structure C 40 and of the general composition $\text{Mo}_2\text{M}(\text{Si}_{1-x}\text{Al}_x)_2$, in which x ranges from 0.1 to 0.6 and M is one or more metals selected from the group consisting of titanium, zirconium, hafnium, tantalum, niobium, vanadium, chromium and tungsten, the quantities of the M-metals being proportioned according to the formula $\text{Mo}_{1-x}\text{M}_x(\text{Si}_{1-x}\text{Al}_x)_2$ in which ranges from zero to a value being at most 0.7.

115 2. A heating element as claimed in Claim 1, in which said sintered body, besides the metallicly conducting particles, consists of a ceramic component constituting from traces to 50% by volume of the solid part of the sintered body.

120 3. A heating element as claimed in Claim 2, in which said ceramic component contains from traces to 40% by weight of SiO_2 in the form of glass, the balance of said component being substantially alumina.

125 4. A heating element as claimed in Claim 2 or 3, in which the ceramic component is

made from an addition of alumina clay constituting from zero to 20% by weight of the sintered body and of bentonite constituting the balance to 20%.

- 5 5. A heating element as claimed in any preceding claim, in which the M-metal is Zr and y at most 0.2.

- 10 6. A heating element as claimed in any one of Claims 1 to 4, in which the M-metal is Ta and y at most 0.7.

7. A heating element as claimed in Claim 6, in which $y=0.05$ and $x=0.2$.

- 15 8. A heating element as claimed in any one of Claims 1 to 4, in which the M-metal is titanium, $y=0.3$ and $x=0.2$.

- 20 9. A heating element as claimed in any preceding claim, in which said sintered body contains boron substances the quantity of boron itself being at most 0.3% by weight of the sintered body.

10. A heating element as claimed in any preceding claim, in which said sintered body is constituted by a surface coating of a thickness of 10 to 500 microns and applied onto

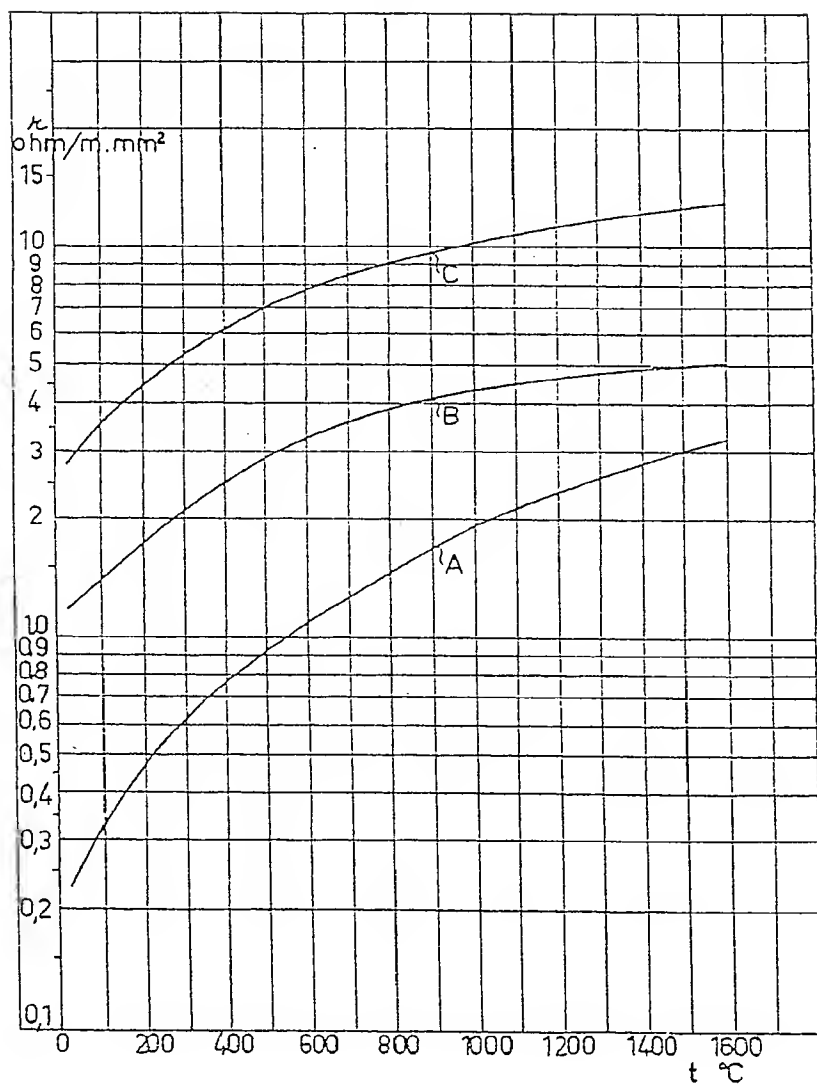
an electrically insulating refractory base member, preferably by employing flame spray metallization techniques. 25

11. A heating element as claimed in any preceding claim, comprising an incandescent heating zone and two terminal end portions, and characterized in that the metallicly conducting component of the incandescent zone is of a composition as stated in Claims 1 to 9, whereas in the terminal end portions the metallicly conducting component consists of tetragonal molybdenum disilicide, the incandescent zone and terminal end portions being of substantially the same cross-sectional areas. 30 35

12. Sintered electric resistance heating elements when produced substantially as described in any one of Examples 1 to 6 herein. 40

For the Applicants,
F. J. CLEVELAND & COMPANY,
Chartered Patent Agents,
29, Southampton Buildings, Chancery Lane,
London, W.C.2.

Fig.1



924497

COMPLETE SPECIFICATION

8 SHEETS

This drawing is a reproduction of
the Original on a reduced scale
Sheets 1 & 2

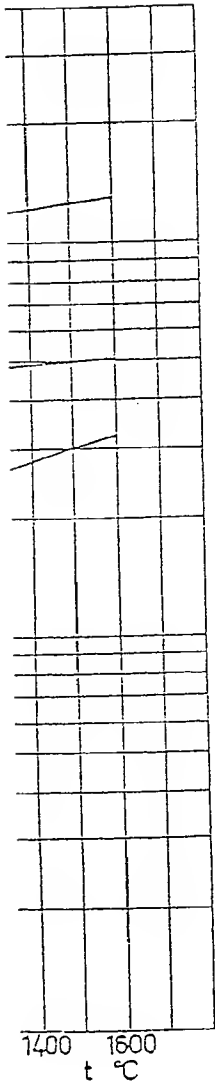


Fig 2

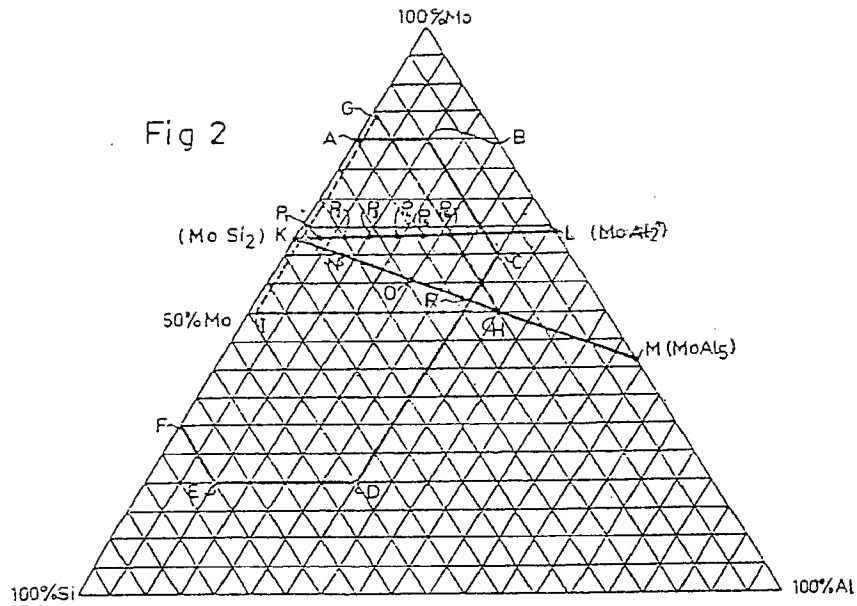


Fig. 1

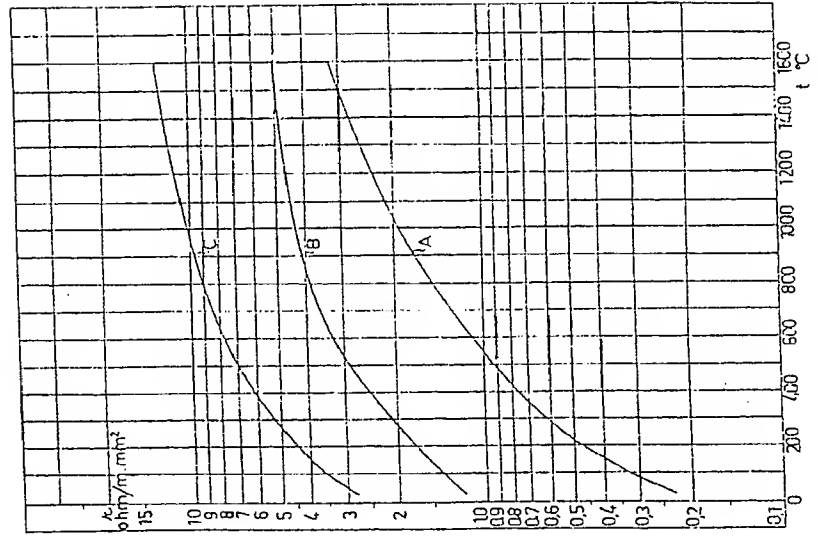


Fig 2

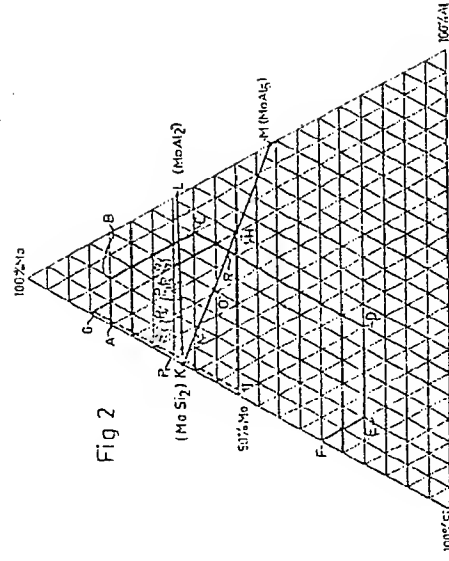


Fig. 3

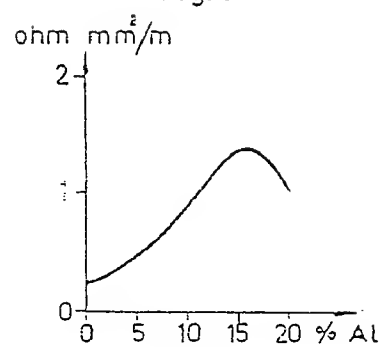
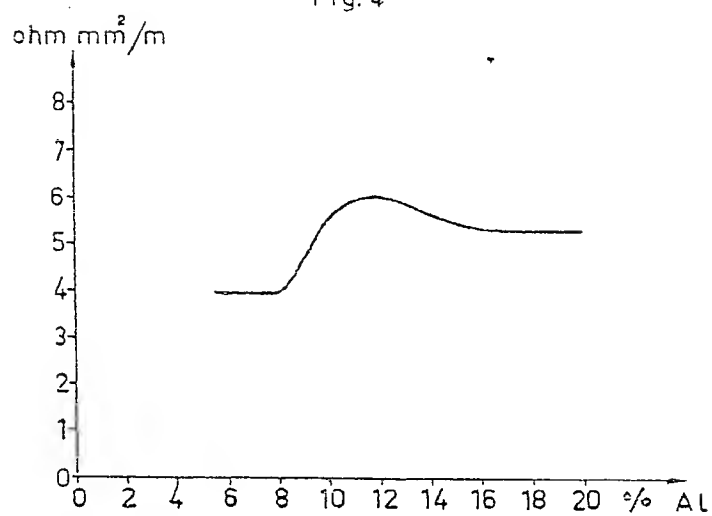


Fig. 4



924497

COMPLETE SPECIFICATION

8 SHEETS

*This drawing is a reproduction of
the Original on a reduced scale*

Sheets 3 & 4

Fig. 5

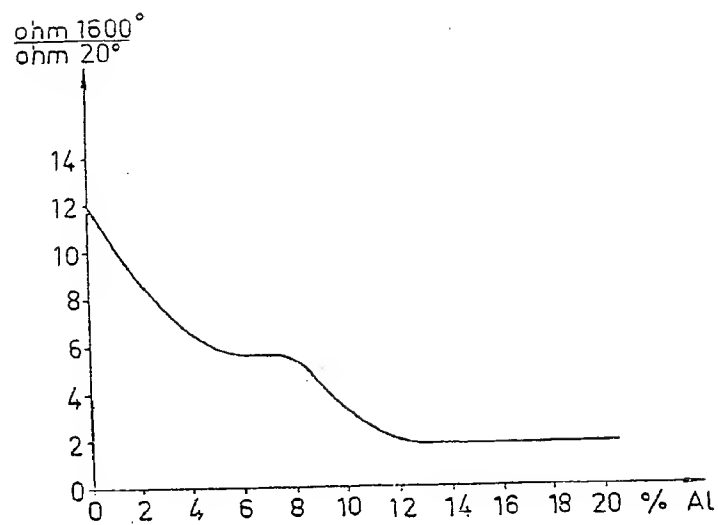


Fig. 3

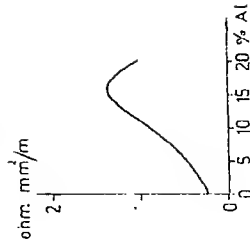


Fig. 4

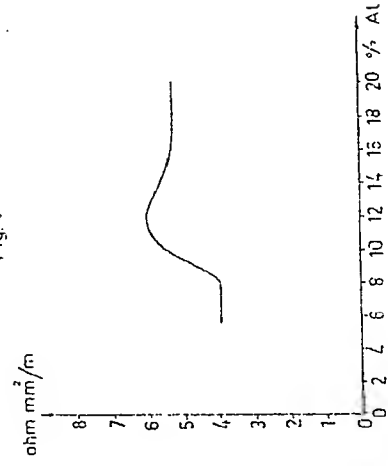


Fig. 5

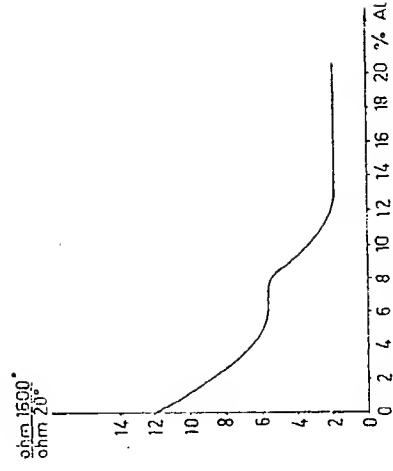


Fig. 6

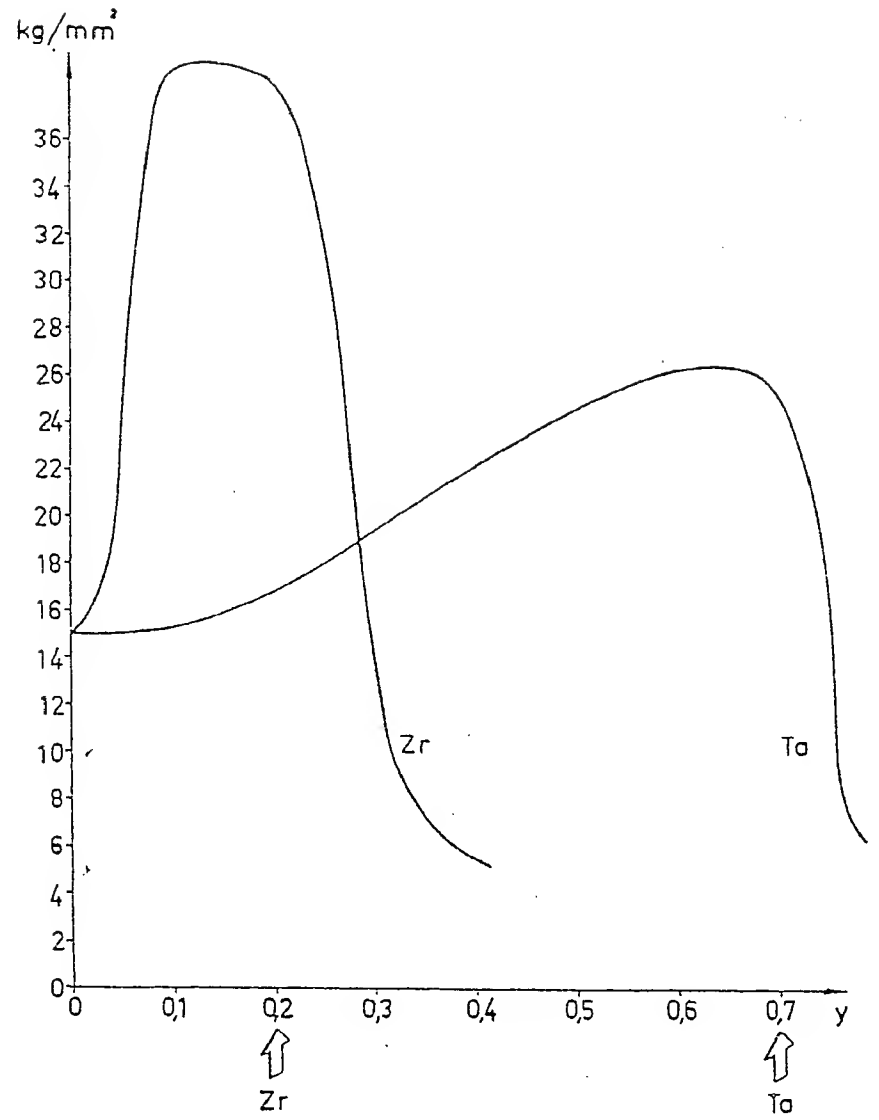


Fig. 7

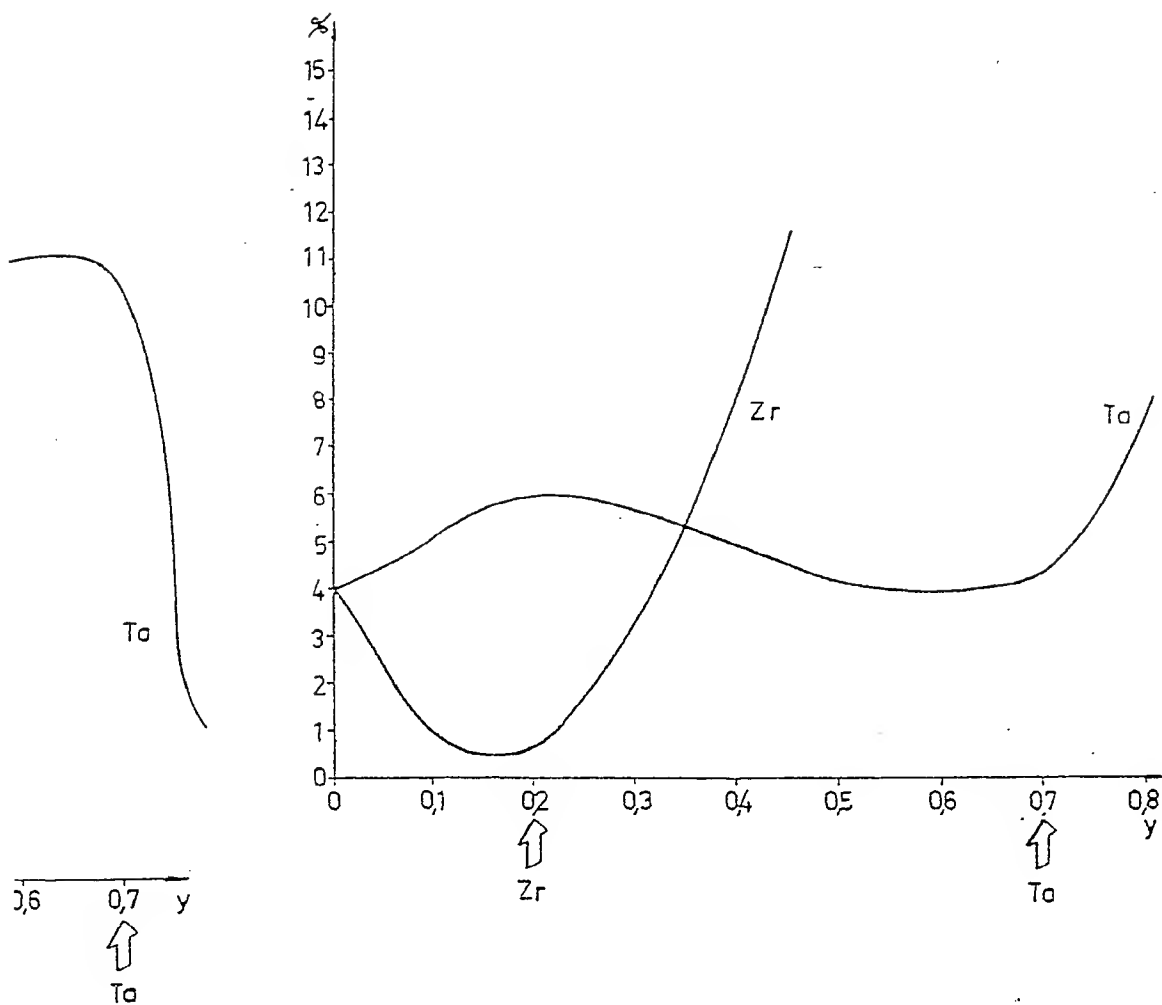


Fig. 6

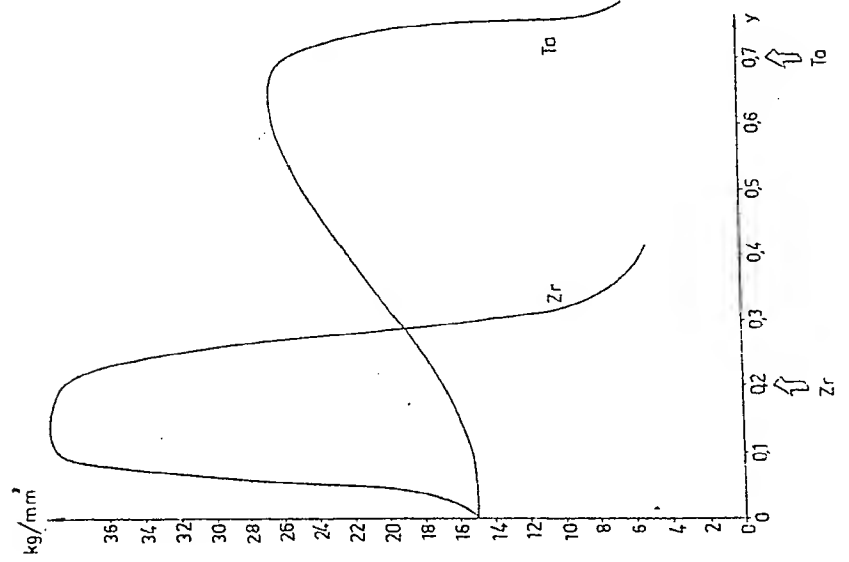
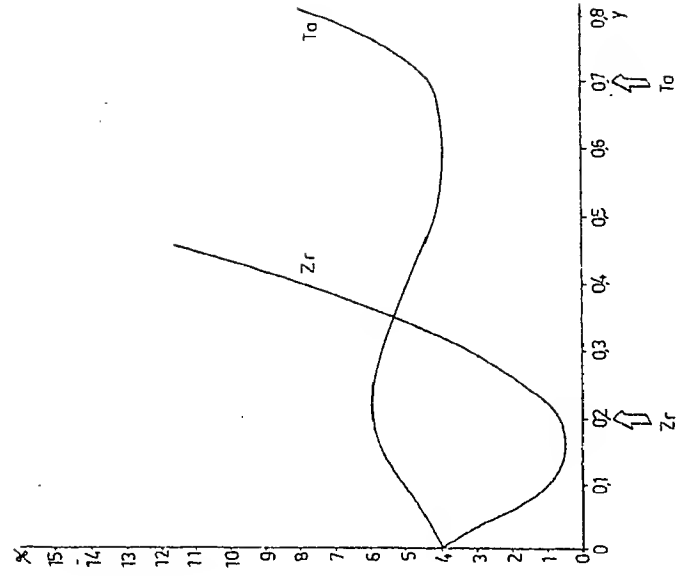
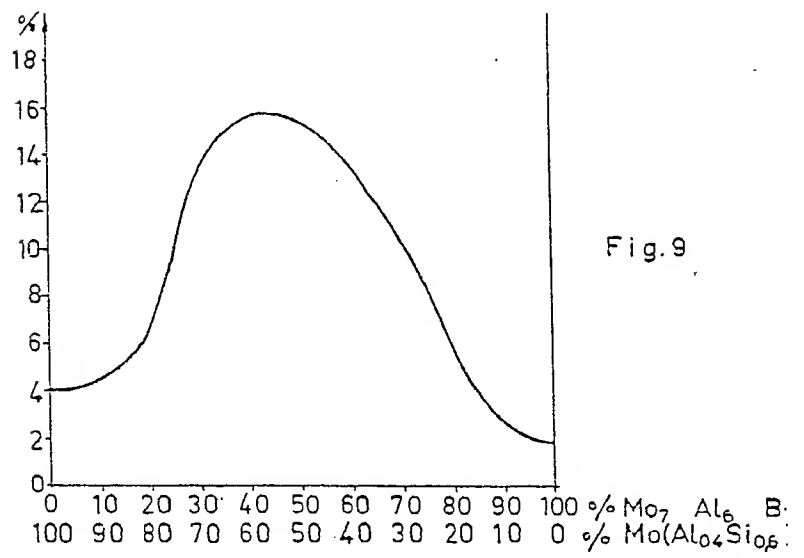
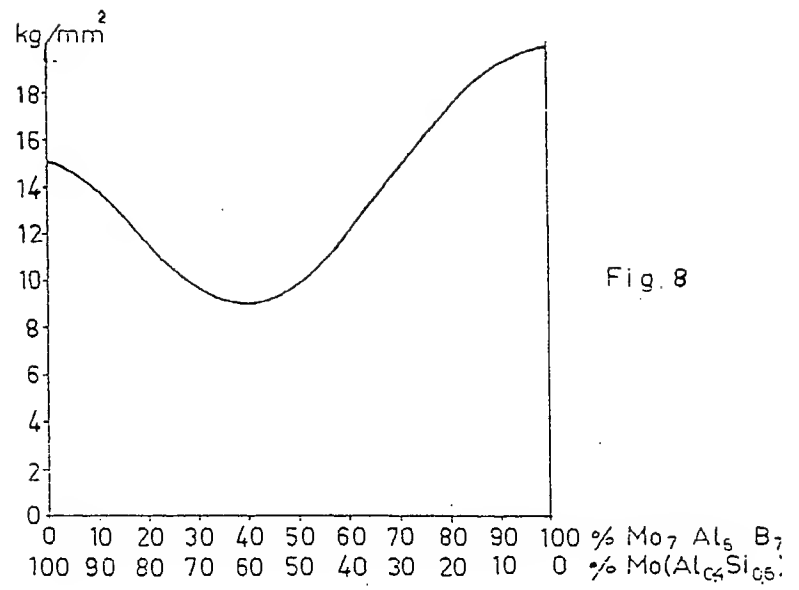


Fig. 7





924497

COMPLETE SPECIFICATION

8 SHEETS

*This drawing is a reproduction of
the Original on a reduced scale
Sheets 7 & 8*

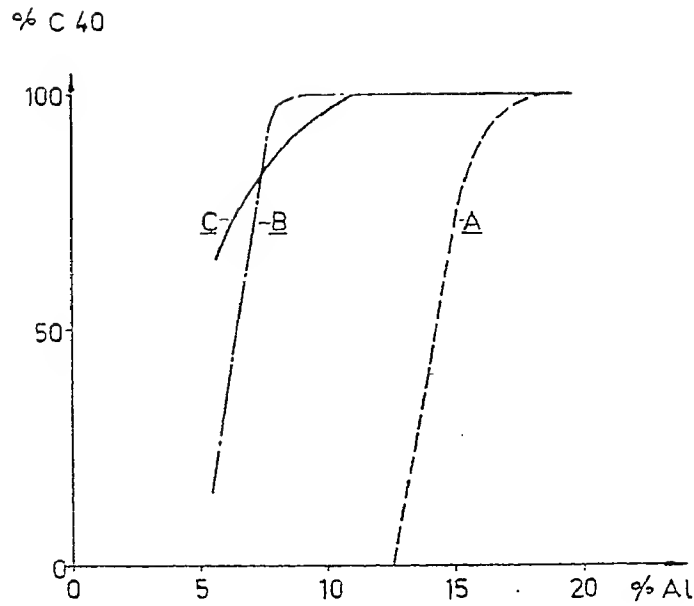
Fig. 8

100 % $\text{Mo}_7\text{Al}_5\text{B}_7$
0 % $\text{Mo}(\text{Al}_{0.4}\text{Si}_{0.6})_2$

Fig. 9

100 % $\text{Mo}_7\text{Al}_5\text{B}_7$
0 % $\text{Mo}(\text{Al}_{0.4}\text{Si}_{0.6})_2$

Fig. 10



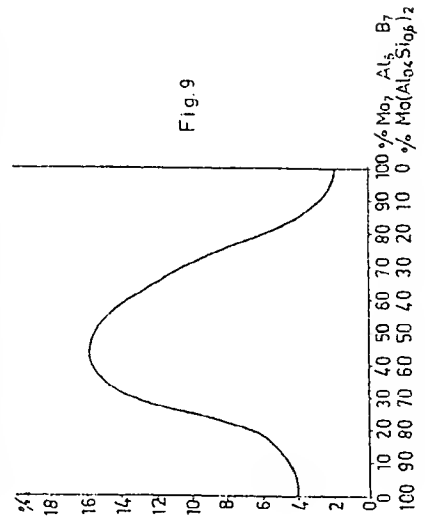
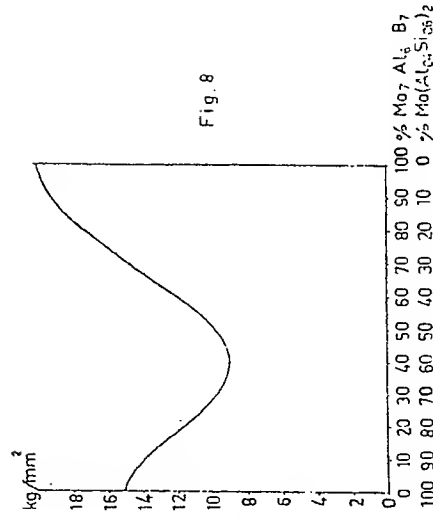
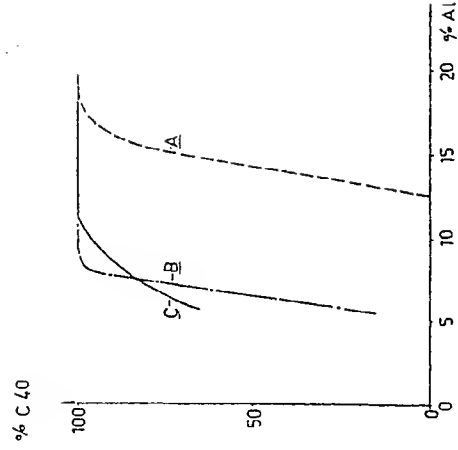


Fig. 10



**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☒ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.